



# **Next Generation Highly Conducting Organic Films Using Novel Donor-Acceptor Molecules for Opto-electronic Applications**

**by Eric Forsythe, Jianmin Shi, and David Morton**

**ARL-TR-5232**

**June 2010**

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14. ABSTRACT <p>This effort continues a two-year Director's Research Initiative (DRI) that investigated various polymer and small molecule mixtures that form the charge transfer (CT) complex to enable next generation highly conducting organic films using novel donor-acceptor molecules for opto-electronic applications. In this DRI, we investigated the CT complexes of 3,4:3',4'-bibenzo[b]thiophene (BBT) with tetracyanoquinodimethane (TCNQ) acceptors. Device data confirmed that the donor-acceptor molecular systems lead to systematic modifications of the charge transport. The thin films were fabricated into devices and I-V properties were studied as a function of annealing. The results demonstrate a 5 to 15 times improvement in the charge transport as a function of annealing. The annealing process apparently contributes to the molecular stack and donor-acceptor alignment. In addition, the ARL-08 molecule (developed by the U.S. Army Research Laboratory [ARL] in the first-year effort) was investigated as an electron transporting layer by doping ARL-08 with a strong electron donating material, low work function metals. The preliminary device data showed interesting characteristics that are being compiled for the patent. In parallel, we investigated ARL's proprietary BBT molecule as a strong donor molecule for CT complexes with TCNQ. The molecular ordering showed a strong molecular stacking that should lead to improved hole transport properties.</p>					
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## 1. Objective

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The Army's transition to lightweight, rugged large area electronics will require novel materials and low-temperature processing on flexible substrates. The Army's need for two-dimensional (2-D) conformal large area electronics includes energy harvesting, information displays, and sensors. The results from this Director's Research Initiative (DRI) will lead to printing of conducting organic materials as a primary build-block that will enable these low-cost, large area applications.

Conducting organic materials are the primary components for Army applications that include large area electronics, solar cells, and information displays, as shown in figure 1. Neutral organic based thin films have equivalent charge mobility to intrinsic amorphous inorganic semiconductor thin films, where the transport is dominated by carrier hopping. However, inorganic semiconductors have a stable, well-defined doping process to improve the charge mobility. Organic semiconductors, to date, have limited examples of doping the host materials to improve charge mobility (1–3). The general program approach is to develop novel organic salts that are doped into a wide range of organic host materials. Organic salts will assist in the charge transfer to the host organic materials similar to doping an inorganic semiconductor. Conducting thin films will improve the device efficiency for a number of applications including photovoltaics, contact doping for thin-film transistors, light emitting devices, and ultimately conducting lines for large area flexible electronics.



Figure 1. Application space for conducting organic materials.

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## 2. Approach

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The novel salts below have been designed and synthesized at the U.S. Army Research Laboratory (ARL). The general concept developed in this DRI is illustrated in equation 1:



where  $[A]^- [B]^+$  is a generic salt that can be thermally sublimed or processed in solution. This salt is then doped into a generic host organic material to demonstrate a conducting thin film.

The experimental approach for the two-year DRI was the investigation of various polymer and small molecule mixtures that form the charge transfer (CT) complex. The focus of the program is twofold. The first focus is the development of polymer based donor-acceptor model CT complexes with polymer donor molecules [Molecule A] with a traditional acceptor molecule, tetracyanoquinodimethane (TCNQ) [Molecule B] (4). This analysis will lead to improved materials designs for next generation material. The second focus of the program is the development of novel CT complexes based on the model CT complexes. In a previous DRI, we found that compounds containing the 3,4:3',4'-bibenzo[b]thiophene (BBT) moiety might provide a class of compounds useful as organic semiconductors (5). In this DRI, we have investigated the CT complexes of BBT with TCNQ acceptors. The synthesis of BBT and its electrical conductivity of its iodine complex were first reported in the late 1970s (6); however, little has been reported on this class of compounds and on its potential as a semiconductor. In addition, a new class of donor molecules was invented in the course of the DRI program.

## **2.1 Polymer Based Donor-acceptor Material**

The following work by post-doc Dr Sanchao Liu has been published in *Synthetic Metals* (4). Here, the novel conducting organic materials based on polycarbazole (PC)/TCNQ complexes were synthesized. The donors chosen are polycarbazoles with electron-donor groups, i.e., carbazole moieties, on the side chains. The TCNQ acceptor molecule can then be inserted between two adjacent donor molecules for increased complex stability. In the first year, we reported on the x-ray crystal structure analysis that showed the formation of a 1:2 CBP:TCNQ complex with donor (carbazole moiety) and acceptor (TCNQ) molecules. During the second year, the polymer CT complexes were tested in device structures consisting of an indium tin oxide (ITO)/CT/magnesium: silver (Mg:Ag) sandwich-like structure. The devices current-voltage (I-V) characteristics were tested with a Keithley 2400 sourcemeter as a function of annealing. The annealing was used to further enable the donor acceptor alignment. Annealing experiments were performed in a glove-box on a hot plate Signature 800 Series from VWR with an aluminum surface. The temperature stability was  $\pm 1\%$  and the overshoot temperature was  $5^\circ\text{C}$ . Thermal annealing was performed on PC/TCNQ complexes, poly(9,9-N-dihexyl-2,7-fluorene-alt-9-phenyl-3,6-carbazole (PHFPC)/TCNQ, and poly(9-vinylcarbazole) (PVK)/TCNQ complexes. A comparison between the annealing effect and complex structures was studied. The polymer donor structures are shown in figure 2.



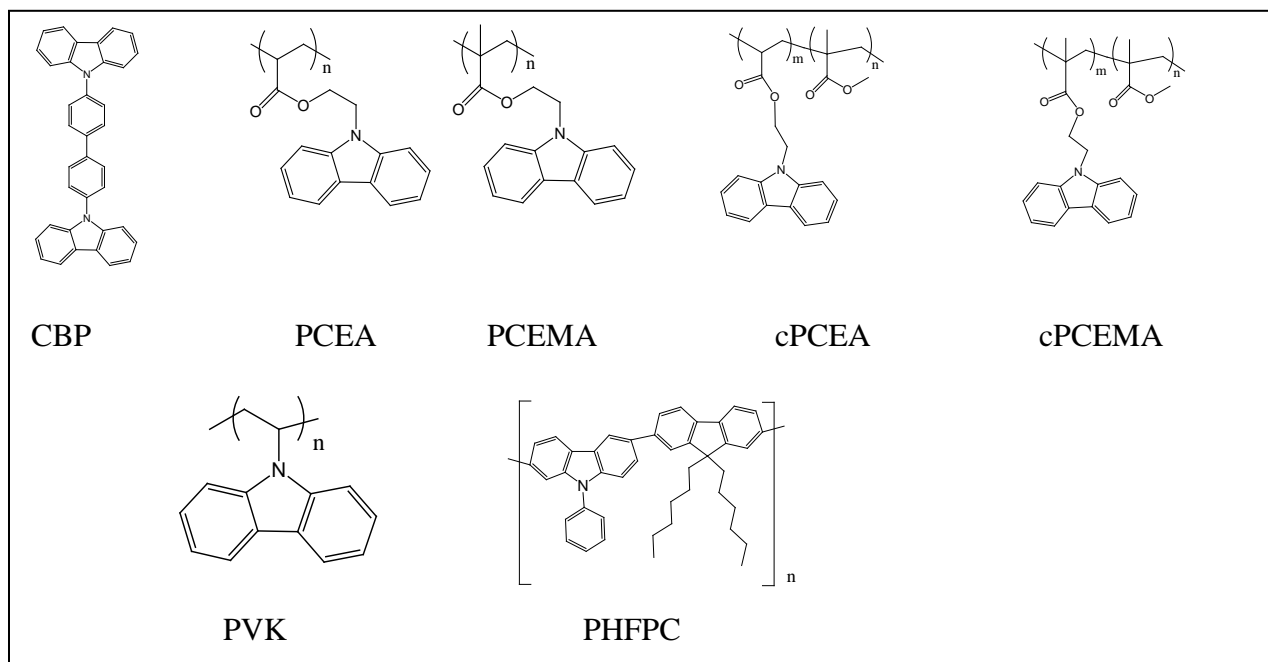


Figure 2. The structures of the donors: CBP: 4,4'-bis(9-carbazolyl)-1,1'-biphenyl; PCEA: poly(9H-carbazole-9-ethyl acrylate); PCEMA: poly(9H-carbazole-9-ethyl methacrylate); cPCEA: poly[(methyl methacrylate)-*co*-(9-H-carbazole-9-ethyl acrylate)], 25% PCEA; cPCEMA: poly[(methyl methacrylate)-*co*-(9-H-carbazole-9-ethyl methacrylate)], 15%PCEMA; PVK: Poly(9-vinylcarbazole); and PHFPC: Poly(9,9-*N*-dihexyl-2,7-fluorene-*alt*-9-phenyl-3,6-carbazole).

## 2.2 Small Molecule Donor-acceptor Molecules

The second experimental aspects of the DRI program focused on the development of small molecule based CT complexes. The molecules investigated are shown in figure 3.

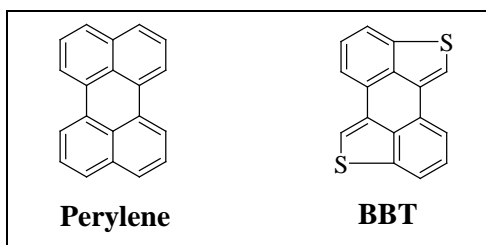


Figure 3. Perylene and BBT molecules study as a function of CT with TCNQ.

### 3. Results

#### 3.1 Polymer Based Donor-acceptor Material

In the DRI program, we investigated the device I-V characteristics of the polymer donor-TCNQ acceptor devices, the ITO/CT complex/Mg:Ag. The devices were tested before and after annealing. Figure 4 shows the I-V characteristics with poly[(methyl methacrylate)-*co*-(9-*H*-carbazole) (cPC), PHFPC, and PVK donor polymers with the TCNQ acceptor.

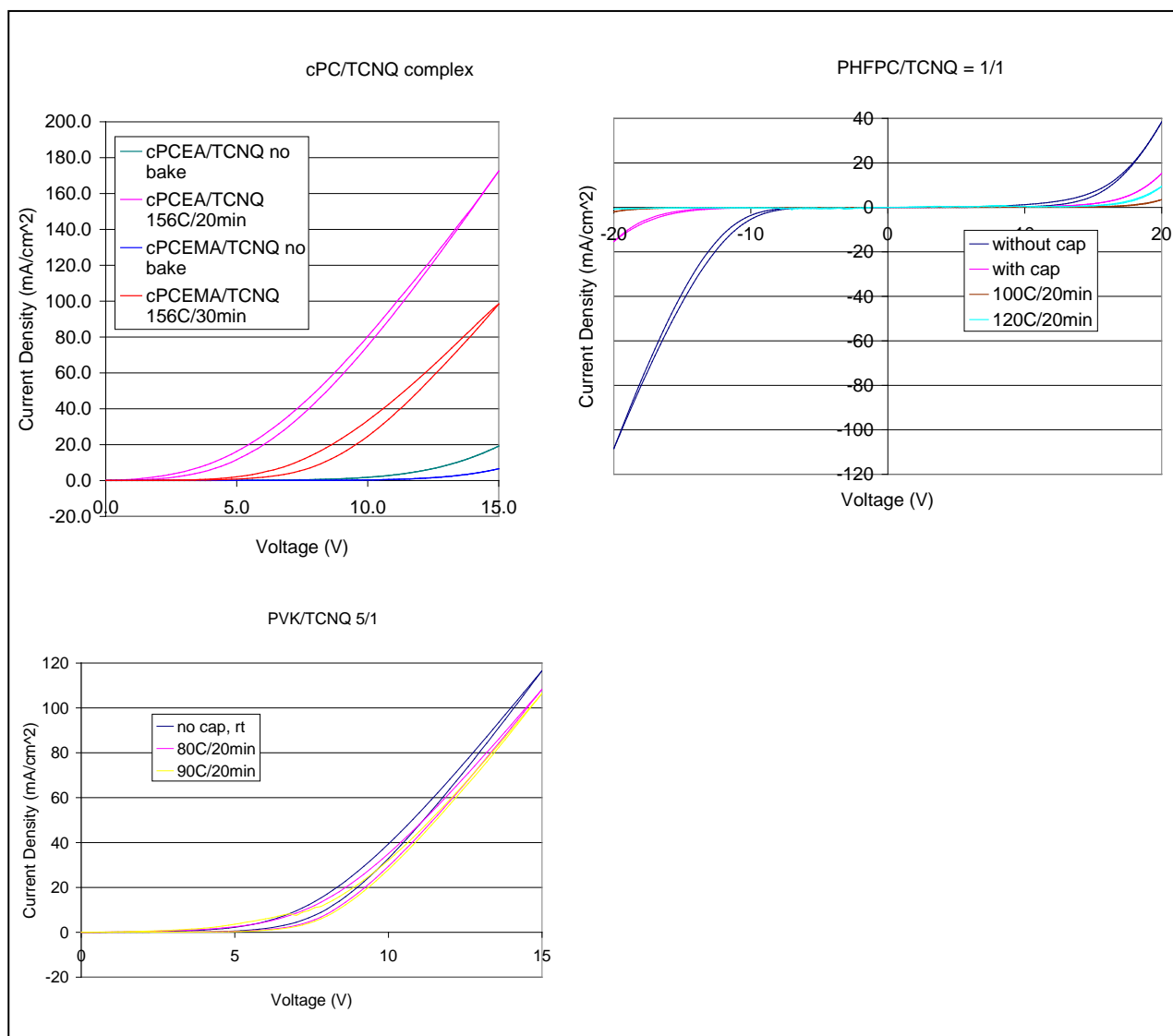


Figure 4. I-V data for the cPC, PHFPC, and PVK donor polymers with the TCNQ acceptor (ITO/CT/Mg:Ag).

### 3.2 Small Molecule Donor-acceptor Molecules

In the first year of the DRI, a new small molecule donor was invented, ARL-08. The patent is in progress. The novel hole transporting material ARL-08 was doped with TCNQ and compared to 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) as well as ARL-08 alone. In figure 5, the devices were fabricated as illustrated in the inset of figure 5a, with the hole transporting layer fabricated on an ITO transparent conducting electrode with an Mg:Ag top electrode. The positive voltage was applied to the ITO contact. These devices clearly demonstrate hole-carrier injection and transport from the ITO contact. We observe an improved hole transport property for the undoped ARL-08 as compared to NPB. The two undoped devices exhibit a space charge region from zero to approximately 2 V, above which the current is injected from the ITO contact and the current dramatically increases. By contrast, the ARL-08 doped with 10% TCNQ demonstrates a continuous hole injection and transport starting at 0 V. In addition, the reverse bias (positive voltage on the Mg:Ag electrode) for the ARL-08:TCNQ devices has a symmetric charge transport as compared to the forward bias; whereas, the undoped ARL-08 and NPB devices have a low leakage space charge current. The doped device results suggest that holes can be injected into the ARL-08:TCNQ organic layer from the low-work function (Mg:Ag) electrode. Clearly, NPB and ARL-08 do not have this property. However, the device results in figure 5 for the ARL-08:TCNQ device do not preclude that electrons could be injected and transported in the organic layer. Based on these findings, the principal investigators (PIs) are filing a patent disclosure to cover the ARL-08 material application for hole injection and improved charge transport.

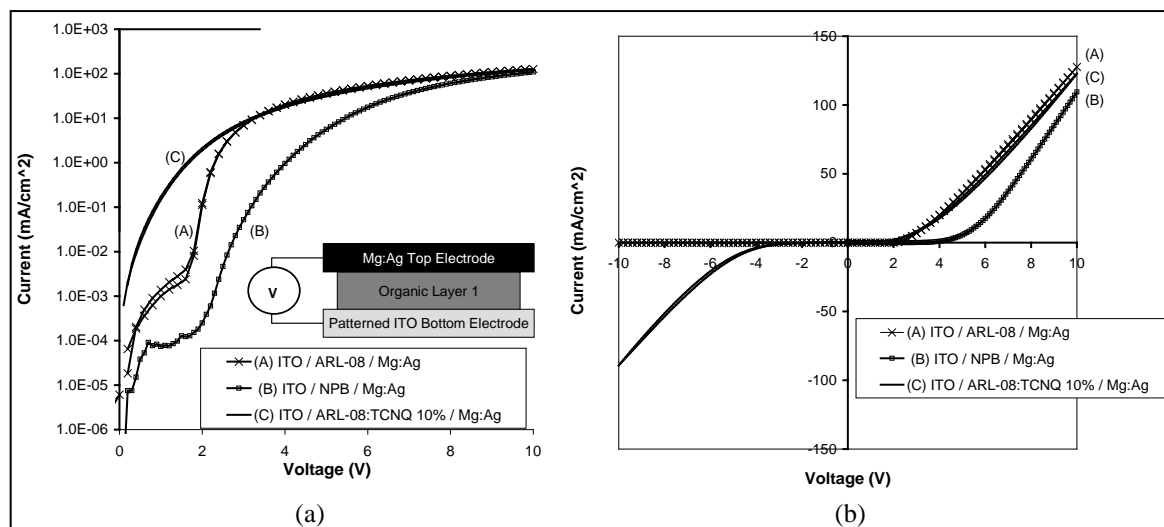


Figure 5. Comparison between the ARL-08 hole transporting layer, the NPB only device, and the ARL-08 doped with 10% TCNQ; (a) is the semi-log plot and (b) is the linear plot for comparison.

In addition to ARL-08, the DRI program investigated the CT complex formation with a BBT donor and a TCNQ acceptor. The BBT-TCNQ complex was prepared by mixing the molecules in dichloromethane solvent at room temperature. The mixture was set at room temperature to let

the solvent slowly evaporate. Needle-like black crystals were obtained. The x-ray diffraction measurements shown in figure 6 were performed at Chemistry and Biochemistry Department, University of Maryland.

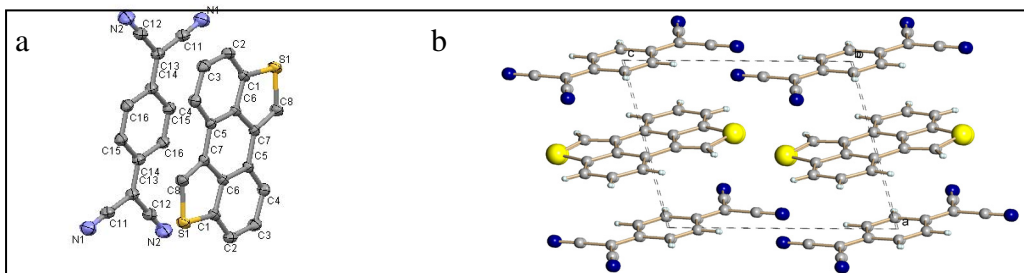


Figure 6. (a) A view of BBT/TCNQ showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 30% probability level. Hydrogen atoms are displayed with an arbitrarily small radius. (b) The packing projected along the *b* axis.

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## 4. Conclusions

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The following DRI represents an important scientific investigation of CT complex molecular systems for improved carrier transport. The CT complexes were investigated as a function of polymer and small molecule systems. For both systems, device data confirmed that the donor-acceptor molecular systems lead to systematic modifications of the charge transport. The polymer systems were used to study the fundamental molecular moieties that contribute to molecular pack and CT formation. The thin films were fabricated into devices and I-V properties were studied as a function of annealing. The results demonstrate a 5 to 15 times improvement in the charge transport as a function of annealing. The annealing process apparently contributes to the molecular stack and donor-acceptor alignment. By comparison, annealing had no effect on device conductivity for the PVK/TCNQ complex up to 140 °C. PVK polymer is not a strong donor polymer. The device data will be published separately.

This DRI developed a new class of small molecule donors with a patent in process. The first year demonstrated the hole transporting characteristics of the CT complexes with TCNQ. During the second year, the ARL-08 molecule was investigated as an electron transporting layer by doping ARL-08 with a strong electron donating material, low work function metals. The preliminary device data showed interesting characteristics that are being compiled for the patent. In parallel, we investigated ARL's proprietary BBT molecule as a strong donor molecule for CT complexes with TCNQ. The molecular ordering showed a strong molecular stacking that should lead to improved hole transport properties. These devices will be investigated further for organic light emitting diode (OLED) and organic photovoltaic applications.

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## 5. References

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1. McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W. M.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nature Materials* **2006**, 5 (4), 328–333.
2. Pfeiffer, M.; et al. *Adv. In Solid State Physics* **1999**, 39, 77–90.
3. Litt, M. H.; Summers, J. W. *J. Polym. Sci. Polym. Chem. Ed.* **1973**, 11, 1359.
4. Liu, S. C.; Shi, J. M.; Forsythe, E. W.; Blomquist, S. M.; Chiu, D. *Synthetic Metals* **2009**, 159 (14), 1438–1442.
5. Shi, J.; Forsythe, E.; Morton, D. U.S. patent application.
6. Wudl, F.; Haddon, R. C.; Zellers, E. T.; Bramwell, F. B. *Org. Chem.* **1979**, 44, 2491–2493.

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## 6. Transitions

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The material and device technology is being formulated into a patent disclosure. This preliminary work has been published in *SPIE Proceedings* and presented in two invited talks and at the FlexTech Alliance Flexible Electronics Conference in 2009. The fundamental research has been published in *Synthetic Metals*, with a follow-on publication in *Advanced Materials*. In parallel, we are working with the Flexible Display Center (FDC) to integrate the ARL-08 molecules and CT complexes with flexible active matrix backplanes and OLEDs. This work will be explored for follow-on intellectual property (IP). We have recently started an American Recovery and Reinvestment Act (ARRA) Stimulus funded program. As a part of this research, the BBT molecule and CT complexes will be scaled and explored for organic photovoltaic applications.

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## List of Symbols, Abbreviations, and Acronyms

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2-D	two-dimensional
ARL	U.S. Army Research Laboratory
ARRA	American Recovery and Reinvestment Act
BBT	3,4:3',4'-bibenzo[b]thiophene
CBP	4,4'-bis(9-carbazolyl)-1,1'-biphenyl
cPC	poly[(methyl methacrylate)- <i>co</i> -(9- <i>H</i> -carbazole)]
cPCEA	poly[(methyl methacrylate)- <i>co</i> -(9- <i>H</i> -carbazole-9-ethyl acrylate)]
cPCEMA	poly[(methyl methacrylate)- <i>co</i> -(9- <i>H</i> -carbazole-9-ethyl methacrylate)]
CT	charge transfer
DRI	Director's Research Initiative
FDC	Flexible Display Center
IP	intellectual property
ITO	indium tin oxide
I-V	current-voltage
Mg:Ag	magnesium: silver
NPB	4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl
OLED	organic light emitting diode
PC	polycarbazole
PCEA	poly(9 <i>H</i> -carbazole-9-ethyl acrylate)
PCEMA	poly(9 <i>H</i> -carbazole-9-ethyl methacrylate)
PHPFC	poly(9,9-N-dihexyl-2,7-fluorene-alt-9-phenyl-3,6-carbazole)
PIs	principal investigators
PVK	poly(9-vinylcarbazole)
TCNQ	tetracyanoquinodimethane

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